

PATENT ABSTRACTS OF JAPAN

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(54) AZOLAKE PIGMENT COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an azolake pigment composition having resistance to souring and capable of giving high gloss.

SOLUTION: This azolake pigment composition is obtained by adding (A) a formaldehyde condensate of 4-aminobenzenesulfonic acid or its salt with a bisphenolic compound or its salt and (B) an acrylic polymer or its sodium salt, potassium salt or ammonium salt in any of a production process of the azolake pigment performed in the turns of a diazotizing reaction process, a coupling reaction process, a lake-making process and an aging process.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About an azo lake pigment constituent, in more detail, this invention is excellent in SOWARINGU-proof nature, and relates to an azo lake pigment constituent which moreover has advanced gloss.

[0002]

[Description of the Prior Art] Since the azo lake pigment is excellent in solvent resistance, lightfastness, etc., it is widely used for each application as a coloring agent of printing ink, a coating, and plastics. In the case of printing ink, especially gravure ink, during preservation or high-speed printing, the viscosity of ink becomes high, or it gels for a short time, and there is a problem it becomes impossible as ink using among these applications. During printing, this phenomenon is considered to be caused by absorbing the moisture in air, and is called the SOWARINGU phenomenon.

[0003] As a means to solve the problem of this SOWARINGU phenomenon, the approach of adding the formaldehyde condensate of 4-aminobenzene sulfonic acid or its salt, and a bisphenols compound or its salt is indicated by invention-in-this-application persons at Japanese Patent Application No. N 89976 [seven to]. However, according to this approach, it was not what has not necessarily sufficient printing ink properties, such as the gloss of printed matter falling or causing a thickening operation with time.

[0004]

[Problem(s) to be Solved by the Invention] Accomplished in order that this invention may solve such a conventional trouble, the purpose of the invention in this application has SOWARINGU-proof nature, and is to offer the azo lake pigment constituent which can moreover give advanced gloss.

[0005]

[Means for Solving the Problem] this invention person etc. that the trouble of the above-mentioned conventional technique should be solved The result wholeheartedly research, (A) 4-aminobenzene sulfonic acid, the salt and a bisphenols compound, or a formaldehyde condensate with the salt, And (B) acrylic polymer or its sodium salt, potassium salt, or ammonium salt The azo lake pigment constituent added and obtained in which process of the production process of an azo lake pigment is excellent in SOWARINGU-proof nature, and came to complete a header and this invention for the ability to advanced gloss to be given moreover.

[0006] Here, although the production process of an azo lake pigment generally consists of (4) aging processes a (1) diazotization reaction process, (2) coupling reaction processes, and (3) lake chemically-modified degree, the above-mentioned (A) component and the (B) component may be added in which process of above-mentioned (1) - (4). It is thought that these (A) components and the (B) component give SOWARINGU-proof nature and advanced gloss by adsorbing the particle of an azo lake pigment and changing the property of the front face.

[0007]

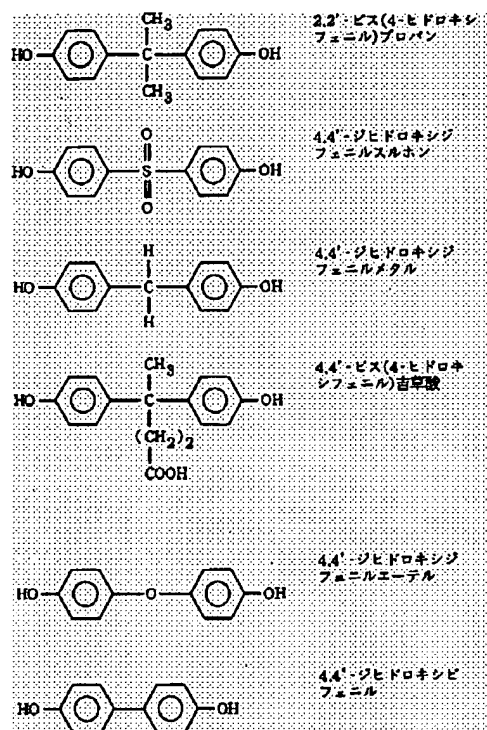
[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained. As an azo lake pigment as used in the field of this invention, it is well-known C.I. Pigment Red conventionally. There are 48 systems, said 49 systems, said 52 systems, said 53 systems, said 57 systems, said 58 systems, said 63 systems, etc., and the manufacture approach also applies to a well-known approach correspondingly conventionally.

[0008] This invention has the description as mentioned above to add (A) 4-aminobenzene sulfonic acid, the salt and a bisphenols compound or a formaldehyde condensate with the salt and (B) acrylic polymer or its sodium salt, potassium salt, or ammonium salt, and to be obtained on the occasion of manufacture of an azo lake pigment.

[0009] (A) What was indicated by JP, 6-60041, B about the water reducing agent for cement as a condensate of a component, and the same thing can be used. That is, this condensate is obtained by carrying out condensation of the mixture of 4-aminobenzene sulfonic acid or its salt, and a bisphenols compound or its salt to the bottom of existence of formaldehyde. As a bisphenols compound, as shown in ** 3, here, for example 2 and 2-screw (4-hydroxyphenyl) propane, 4, and 4'-dihydroxy diphenylsulfone, A - dihydroxy diphenylmethane, and 4 and 4' 4, 4'-screw (4-hydroxyphenyl) valeric acid - dihydroxy diphenyl ether, and 4 and 4' 4, 4'-dihydroxydiphenyl can be mentioned, and there is bis-parsing P121,125,215,235 (all are a bisphenol sulfonic-acid system condensate and/or its Na salt) by Nippon Paper Industries Co., Ltd. as a commercial item.

[0010]

[Formula 3]

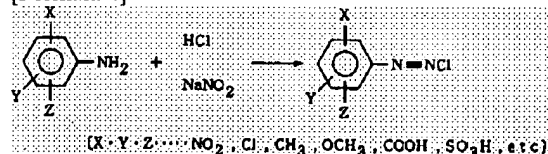


[0011] Moreover, as a (B) component, these sodium salt, potassium salt, and ammonium salt can be used for a styrene-maleic-acid copolymer, polymer lane acid, polyacrylic acid, and polyacrylic acid-acrylic-acid ammonium salt copolymer, an acrylic-acid-maleic-acid copolymer, the acrylic polymer of a styrene-acrylic-acid copolymer, and a list. Moreover, the copolymer of acrylic-acid-acrylic-acid sodium salt, the copolymer of acrylic-acid-acrylic-acid potassium salt, the copolymer of acrylic-acid-acrylic-acid ammonium salt, etc. can be mentioned as a (B) component. (B) As a commercial item which can be used as a component For example, Aron A-6330 (acrylic-acid 1 maleic-acid copolymer) made from Toagosei Chemical industry, Aron A-6270 (acrylic-acid-acrylic-acid ammonium salt copolymer), the Dai-Ichi Kogyo Seiyaku Co., Ltd. make -- De Dis coat KS-140 (sodium salt of a styrene-maleic-acid monoester copolymer) -- made in [Johnson Polymer] the De Dis coat N-14 (ammonium salt of a styrene-maleic-acid monoester copolymer) -- there are JON krill 61J (styrene acrylic resin water solution), a JON krill 52 (styrene acrylic resin water solution), etc.

[0012] Below, this azo lake pigment constituent is explained concretely. The desirable azo lake pigment constituent of this invention is manufactured by the manufacture approach illustrated below. First, as shown in ** 4, the aromatic series primary amine which has (1) carboxyl group or a sulfonic group diazotized according to a conventional method.

[0013]

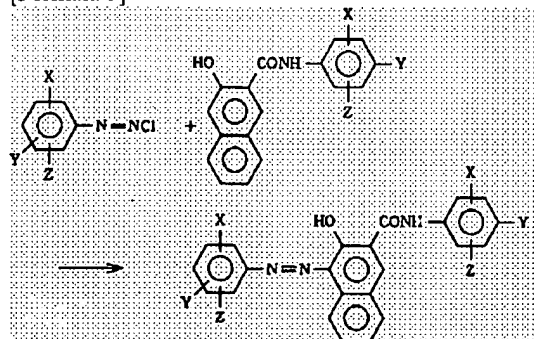
[Formula 4]



[0014] Next, as shown in ** 5, coupling is carried out to coupling components, such as (2) beta-naphthol and beta-oxynaphthoic acid, and the alkali-metal salt of a water-soluble or poorly soluble color is obtained.

[0015]

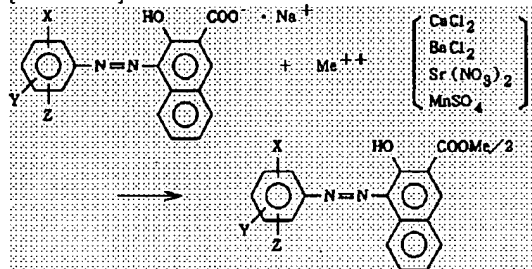
[Formula 5]



[0016] As shown in ** 6, this is made to add and lake-ize polyvalent metal ion, such as (3) alkaline earth metal and manganese, and the azo pigment of water-insoluble nature is obtained to it. Subsequently, (4) aging processing is performed and an azo lake pigment is obtained.

[0017]

[Formula 6]



[0018] The azo lake pigment constituent of this invention is characterized by adding the (A) component and the (B) component at one process of above-mentioned production process (1) - (4), processing, and being obtained to the azo lake pigment to generate. That is, (A) and the (B) component may be added among the water solution of a diazo component in any of the pigment suspension middle class in the pigment suspension in the color solution the water solution of a coupling component, and after coupling, and after lake-izing, and after aging processing. It is desirable to add (A) and the (B) component in the pigment suspension under aging processing among these addition stages.

[0019] The desirable addition of the condensate of the (A) component of this invention is the 0.5 - 10.0 weight section to the azo lake pigment 100 weight section, and the acrylic polymer of the (B) component or the desirable addition of the salt is the 0.1 - 20.0 weight section to the azo lake pigment 100 weight section.

[0020]

[Example] It is not limited by these, although it has an example in below and this invention is further explained to it at a detail. In addition, as long as there is no notice especially, in each following example, there are weight criteria with the "section" or "%."

[0021] (Example 1) 2. - 1000g of water was made to distribute chloro-4-toluidine-5-sulfonic-acid soda 50g (0.21 mols), ice was added, it was set as 0-5-degree C temperature conditions, 55g of HCl water solutions was added 35%, and it agitated for 20 minutes. Then, the diazo compound was obtained by adding 90g (0.39 mols) of sodium nitrite water solutions 30%, and agitating for 60 minutes.

[0022] Subsequently, with 17g (0.43 mols) of sodium hydroxides, it was made to dissolve in 1000g of water, and 40g (0.21 mols) of beta-oxynaphthoic acid was used as the coupling solution. The above-mentioned diazo compound was added on temperature conditions 5 degrees C or less in this solution, the coupling reaction was performed, and azo dye suspension was obtained.

[0023] 5g of bis-parsing P125 (a bisphenol sulfonic-acid system condensate and/or its Na salt) was added as a (A) component, further, as a (B) component, 5g added to this azo dye suspension, and Aron A-6330 (acrylic-acid 1 maleic-acid copolymer) was agitated for 30 minutes to it. Then, the temperature up was carried out to 60 degrees C, 200g (0.24 mols) of strontium-nitrate water solutions was added 25%, lake-ization was performed, it agitated for 30 more minutes, and the lake-ized reaction was ended. The temperature up was carried out and it was made to **** for 60 minutes to 90 degrees C after lake-ized reaction termination. After filtering and rinsing this reaction mixture, it was made to dry at 100 degrees C, and about 110g (0. mols) of azo lake pigment constituents of this invention was obtained.

[0024] (Example 1 of a comparison) In the example 1, addition of Aron A-6330 of the (B) component was excluded, and also about 107g (content of 0.2 mols of a pigment) of azo lake pigments was obtained by the same conditions as an example 1, and identity operation.

[0025] (Example 2) 1000g of water was made to distribute 50g (0.22 mols) of 2-aminonaphthalene-1-sulfonic acids, ice was added, it was set as 0-5-degree C temperature conditions, 55g of HCl water solutions was added 35%, and it agitated for 20 minutes. Then, it is ***** about a diazo compound by adding 90g (0.39 mols) of sodium nitrite water solutions 30%, and stirring for 60 minutes.

[0026] Subsequently, with 15g (0.38 mols) of sodium hydroxides, it was made to dissolve in 1000g of water, and 33g (0.23 mols) of beta-naphthol was used as the coupling solution. The above-mentioned diazo compound was added on temperature conditions 5 degrees C or less in this solution, the coupling reaction was performed, and azo dye suspension was obtained.

[0027] The temperature up of this azo dye suspension was carried out to 50 degrees C, 120g (0.12 mols) of barium chloride water solutions was added 25%, lake-ization was performed, it agitated for 30 more minutes, and the lake-ized reaction was ended. a lake --izing -- a reaction -- termination -- aft -- 90 -- degree C -- up to -- a temperature up -- carrying out -- 60 -- a minute -- between -- having riped -- after -- (-- A --) -- a component -- ***** -- bis-- parsing -- P -- 215 (a bisphenol sulfonic-acid system condensate and/or its Na salt) -- eight -- g -- adding -- further -- (-- B --) -- a component -- ***** -- De Dis -- a coat -- KS - 140 (sodium salt of a styrene-maleic-acid monoester copolymer) -- four -- g -- adding -- 30 -- a minute -- between -- riping -- having made . After filtering and rinsing this reaction mixture, it was made to dry at 100 degrees C, and about 98g (0.11 mols) of pigments of a pigment) of azo lake pigment constituents of this invention was obtained.

[0028] (Example 2 of a comparison) In the example 2, addition of the (B) component of De Dis coat KS-140 was excluded, and also about 95g (0.11 mo of azo lake pigments was obtained by the same conditions as an example 2, and identity operation.

[0029] (Example 3) 1000g of water was made to distribute 50g (0.23 mols) of 3-amino-6-chloro toluene-4-sulfonic acids, ice was added, it was set as 0-5-degree C conditions, 55g of HCl water solutions was added 35%, and it agitated for 20 minutes. Then, the diazo compound was obtained by adding 90g (0.39 mols) of sodium nitrite water solutions 30%, and agitating for 60 minutes.

[0030] Subsequently, with 15g (0.38 mols) of sodium hydroxides, it was made to dissolve in 1000g of water, and 30g (0.21 mols) of beta-naphthol was used as the coupling solution. In this solution, 6g of bis-parsing P235 (a bisphenol sulfonic-acid system condensate and/or its Na salt) was added as a (A) component, further, as a (B) component, 6g added and Aron A-6270 (acrylic-acid-acrylic-acid ammonium salt copolymer) was agitated. Next, the above-mentioned diazo compound was added on temperature conditions 5 degrees C or less, the coupling reaction was performed, and azo dye suspension was obtained.

[0031] The temperature up of this azo dye suspension was carried out to 50 degrees C, 70g (0.12 mols) of calcium chloride water solutions was added 25%, lake-ization was performed, it agitated for 30 more minutes, and the lake-ized reaction was ended. The temperature up was carried out and it was made to ripe for 30 minutes to 90 degrees C after lake-ized reaction termination. After filtering and rinsing reaction mixture, it was made to dry at 100 degrees C, and about 90g (0.11 mols) of azo lake pigment constituents of this invention was obtained.

[0032] (Example 3 of a comparison) In the example 3, addition of Aron A-6270 of the (B) component was excluded, and also about 87g (0.11 mols) of AZORE-KI pigments was obtained by the same conditions as an example 3, and identity operation.

[0033] (Example 4) The diazo compound was obtained by making 1000g of water distribute 50g (0.27 mols) of 4-toluidine-3-sulfonic acids, adding ice, setting it as 0-5-degree C temperature conditions, adding 60g of HCl water solutions 35%, agitating for 20 minutes, adding 95g (0.41 mols) of sodium nitrite water solutions 30% after that, and agitating for 60 minutes.

[0034] Subsequently, with 22g (0.55 mols) of sodium hydroxides, it was made to dissolve in 1000g of water, and 50g (0.27 mols) of beta-oxynaphthoic acid was used as the coupling solution. The above-mentioned diazotation component was added on temperature conditions 5 degrees C or less in this solution, the Cobb ring reaction was performed, and azo dye suspension was obtained.

[0035] The temperature up of this azo dye suspension was carried out to 60 degrees C, 160g (0.27 mols) of calcium chloride water solutions was added 25%, lake-ization was performed, it agitated for 30 more minutes, and the lake-ized reaction was ended. After lake-ized reaction termination, to 85 degrees C, the temperature up was carried out and it riped for 30 minutes. Then, 4g of bis-parsing P121 (a bisphenol sulfonic-acid system condensate and/or its Na salt) is added as a (A) component, further, as a (B) component, 5g added and JON krill 61J (styrene acrylic resin water solution) were ripened for 30 minutes. After filtering and rinsing reaction mixture, it was made to dry at 100 degrees C, and about 110g (0.26 mols) of azo lake pigments of this invention was obtained.

[0036] (Example 4 of a comparison) In the example 4, addition of the (B) component of JON krill 61J was excluded, and also about 106g (0.25 mols) of azo lake pigments was obtained by the same conditions as an example 4, and identity operation.

[0037] (Preparation of example of trial-printing ink) Next, the thing for which the component shown in Table 1 and 2 using the azo lake pigment constituent obtained in examples 1-4 and the examples 1-4 of a comparison is distributed for 30 minutes with a paint conditioner, Polyamide nitrocellulose system gravure ink (the examples 1-4 of a trial and examples 1-4 of a comparative study) and polyurethane system gravure ink (the examples 5-8 of a trial and examples 5-8 of a comparative study) were prepared.

[0038]

[Table 1]

ポリアミド・ニトロセルロース系グラビア印刷インキ

(試験例1～4、比較試験例1～4)

アゾレーキ顔料組成物	10部
ポリアミドワニス	45部
硝化綿ワニス	30部
シンナー (トルエン、IPA、酢エチ)	15部
ガラスビーズ (3mmφ)	200部

[0039]

[Table 2]

ポリウレタン系グラビア印刷インキ

(試験例5～8、比較試験例5～8)

アゾレーキ顔料組成物	12部
ポリウレタン系ワニス	50部
シンナー (トルエン、IPA、MEK)	50部
ガラスビーズ (3mmφ)	200部

[0040] (Evaluation trial of printing ink) About the printing ink of the examples 1-8 of a trial prepared above, and the examples 1-8 of a comparative study the viscosity immediately after preparation was measured by the Brookfield viscometer.

[0041] Next, the water of the 0.5 sections was added to each printing ink 25 section, the paint conditioner distributed for 10 minutes, and the viscosity immediately after distribution was measured. Furthermore, the viscosity after putting the printing ink which added these water for seven days into a 40-degree C thermostat was measured, and aging of ink was investigated.

[0042] Moreover, gloss carried out drawdown of the ink immediately after preparation to PP film, and measured it with the glossmeter (60 degrees of incident angles). The test result of polyamide nitrocellulose system gravure ink and polyurethane system gravure ink was shown in Table 3 and 4, respectively.

[0043]

[Table 3]

ポリアミド・ニトロセルロース系グラビア印刷インキ

	アゾレーキ顔料組成物	調製インキの粘度 (cps)			光沢 (%)
		調製直後	水添加直後	40℃×7日後	
試験例1	実施例1	232	227	256	93
試験例2	実施例2	225	220	232	91
試験例3	実施例3	228	215	245	91
試験例4	実施例4	211	211	221	92
比較例1	比較例1	273	310	764	74
比較例2	比較例2	265	331	823	78
比較例3	比較例3	281	344	1065	69
比較例4	比較例4	282	327	897	69

[0044]

[Table 4]

ポリウレタン系グラビア印刷インキ

	アゾレーキ顔料組成物	調製インキの粘度 (cps)			光沢 (%)
		調製直後	水添加直後	40℃×7日後	
試験例5	実施例1	154	154	201	86
試験例6	実施例2	158	150	181	87
試験例7	実施例3	160	159	169	90
試験例8	実施例4	143	144	175	89
比較例5	比較例1	223	278	885	73
比較例6	比較例2	201	290	901	78
比較例7	比較例3	245	323	1105	67
比較例8	比較例4	220	281	947	72

[0045] As shown in Table 3, the polyamide nitrocellulose system gravure ink of the examples 1-4 of a trial which used the azo lake pigment constituent examples 1-4 showed the numeric value also with high gloss when the increment in viscosity is not seen and carries out drawdown to PP film also in an immediately after ink preparation and water addition distribution and after the preservation 40 degrees C during seven days. On the other hand, the increment in viscosity was seen a little by addition distribution of water, and, as for the polyamide nitrocellulose system gravure ink of the examples 1-4 of a comparative study which used the azo lake pigment constituent of the examples 1-4 of a comparison, the remarkable increment in viscosity was seen by preservation 40 degrees C for seven days. Moreover, gloss was also low as compared with the examples 1-4 of a trial.

[0046] Moreover, although the increment in viscosity was not seen [in / in the polyurethane system gravure ink of the examples 5-4 of a trial which use the azo lake pigment constituent of examples 1-4 / any immediately after ink preparation and water addition distribution] but some viscosity rise was seen after the preservation 40 degrees C during seven days as shown in Table 4, rise width of face was slight. Moreover, the numeric value also with the high gloss at the time of carrying out drawdown was shown in PP film. On the other hand, the increment in viscosity was seen a little by addition distribution of water, and, as for the polyurethane system gravure ink of the examples 5-8 of a comparative study which used the azo lake pigment constituent of the examples 1-4 of a comparison, the remarkable increment in viscosity was seen by preservation 40 degrees C for seven days. Moreover, gloss was also low as compared with the examples 4-8 of a trial.

[0047]

[Effect of the Invention] When it is used as printing ink, during preservation or high-speed printing, the viscosity of ink becomes high for a short time, and the azo lake pigment constituent of this invention is gelled, and it does not become impossible as ink using it. Moreover, the printed matter using this printing ink has advanced gloss. Therefore, the azo lake pigment constituent of this invention is very useful as a pigment for gravure ink.

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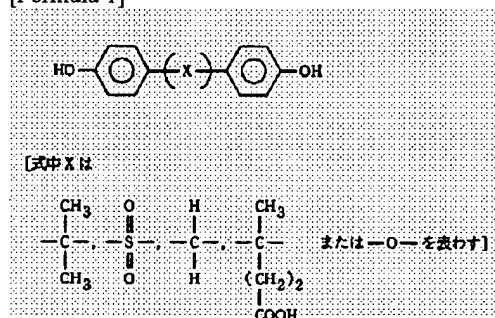
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CLAIMS

- [Claim(s)]
- [Claim 1] The azo lake pigment constituent characterized by setting they being [any of the production process of an azo lake pigment], adding (A) 4-aminobenzene sulfonic acid or its salt, a bisphenols compound or a formaldehyde condensate with the salt and (B) acrylic polymer or its sodium sa and potassium salt, or ammonium salt, and being obtained.
- [Claim 2] The azo lake pigment constituent according to claim 1 characterized by the bisphenols compound in the aforementioned (A) component being compound expressed with the formation 1 of the following general formula, or ** 2.
- [Formula 1]



- [Claim 3] The aforementioned (B) component A styrene-maleic-acid copolymer, a polymer lane acid, A polyacrylic acid and polyacrylic acid-acrylic-aci ammonium salt copolymer, An acrylic-acid-maleic-acid copolymer, the acrylic polymer of a styrene-acrylic-acid copolymer, In a list, the copolymer of these sodium salt, potassium salt and ammonium salt, and acrylic-acid-acrylic-acid sodium salt, The copolymer of acrylic-acid-acrylic-acid potassium sa the azo lake pigment constituent according to claim 1 or 2 characterized by being the compound chosen from the group which becomes a list from the copolymer of acrylic-acid-acrylic-acid ammonium salt.
- [Claim 4] An azo lake pigment constituent given in claim 1 thru/or any of 3 they are. [to which the aforementioned (A) component is characterized by existing at 0.5 - 10.0% of the weight of a rate to an azo lake pigment]
- [Claim 5] An azo lake pigment constituent given in claim 1 thru/or any of 4 they are. [to which the aforementioned (B) component is characterized by existing at 0.1 - 20.0% of the weight of a rate to an azo lake pigment]
- [Claim 6] The printing ink constituent containing an azo lake pigment constituent given in any [claim 1 thru/or] of 5 they are.

[Translation done.]